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## APPLICATION FOR PATENT

Inventor: JO ANN M. CANICH

Title: PROCESS FOR PRODUCING CRYSTALLINE  
POLY- $\alpha$ -OLEFINS WITH A MONOCYCLOPENTADIENYL  
TRANSITION METAL CATALYST SYSTEM

*ans*  
*ait*  
SPECIFICATION

5 This application is a Continuation-in-Part of United States Patent Application Serial No. 533,245 filed June 4, 1990 which in turn is a continuation-in-part of United States Patent Application Serial No. 406,945 filed September 13, 1989. *And now abandoned*

*B*  
FIELD OF THE INVENTION

*B* 10 This invention relates to a process for polymerizing  $\alpha$ -olefins which utilize<sup>s</sup> certain monocyclopentadienyl metal compounds of a Group IV B transition metal of the Periodic Table of Elements in an alumoxane activated catalyst system to produce crystalline poly- $\alpha$ -olefins, particularly polypropylene and  $\alpha$ -olefin copolymers of propylene.

15 BACKGROUND OF THE INVENTION

20 As is well known, various processes and catalysts exist for the homopolymerization or copolymerization of olefins. For many applications it is of primary importance for a polyolefin to have a high weight average molecular weight while having a relatively narrow molecular weight distribution. A high weight average molecular weight, when accompanied by a narrow molecular weight distribution, provides a polyolefin with high

25 strength properties.

Traditional Ziegler-Natta catalysts systems -- a transition metal compound cocatalyzed by an aluminum alkyl -- are capable of producing polyolefins having a

high molecular weight but a broad molecular weight distribution.

5 More recently a catalyst system has been developed wherein the transition metal compound has two or more cyclopentadienyl ring ligands -- such transition metal compound being referred to herein as a "metallocene" -- which catalyzes the production of olefin monomers to polyolefins. Accordingly, titanocenes and zirconocenes, have been utilized as the transition metal component in  
10 such "metallocene" containing catalyst system for the production of polyolefins and ethylene- $\alpha$ -olefin copolymers. When such metallocenes are cocatalyzed with an aluminum alkyl -- as is the case with a traditional type Ziegler-Natta catalyst system -- the catalytic  
15 activity of such metallocene catalyst system is generally too low to be of any commercial interest.

It has since become known that such metallocenes may be cocatalyzed with an alumoxane -- rather than an aluminum alkyl -- to provide a metallocene catalyst  
20 system of high activity for the production of polyolefins.

*B* The zirconocenes, as cocatalyzed or activated with an alumoxane, are commonly more active than their hafnium or titanium analogues <sup>new</sup> for the polymerization of ethylene alone or together with an  $\alpha$ -olefin comonomer. When  
25 employed in a non-supported form -- i.e., as a homogeneous or soluble catalyst system -- to obtain a satisfactory rate of productivity even with the most active zirconocene species typically requires the use of a quantity of alumoxane activator sufficient to provide  
30 an aluminum atom to transition metal atom ratio (Al:TM) of at least greater than 1000:1; often greater than 5000:1, and frequently on the order of 10,000:1. Such quantities of alumoxane impart to a polymer produced with  
35 such catalyst system an undesirable content of catalyst

metal residue, i.e., an undesirable "ash" content (the nonvolatile metal content). In high pressure polymerization procedures using soluble catalyst systems wherein the reactor pressure exceeds about 500 bar only the zirconium or hafnium species of metallocenes may be used. Titanium species of metallocenes are generally unstable at such high pressures unless deposited upon a catalyst support. A wide variety of Group IV B transition metal compounds have been named as possible candidates for an alumoxane cocatalyzed catalyst system. Although bis(cyclopentadienyl) Group IV B transition metal compounds have been the most preferred and heavily investigated for use in alumoxane activated catalyst systems for polyolefin production, suggestions have appeared that mono and tris(cyclopentadienyl) transition metal compounds may also be useful. See, for example U.S. Patent Nos. 4,522,982; 4,530,914 and 4,701,431. Such mono(cyclopentadienyl) transition metal compounds as have heretofore been suggested as candidates for an alumoxane activated catalyst system are mono(cyclopentadienyl) transition metal trihalides and trialkyls.

More recently, International Publication No. WO 87/03887 describes the use of a composition comprising a transition metal coordinated to at least one cyclopentadienyl and at least one heteroatom ligand as a transition metal component for use in an alumoxane activated catalyst system for  $\alpha$ -olefin polymerization. The composition is broadly defined as a transition metal, preferably of Group IV B of the Periodic Table, which is coordinated with at least one cyclopentadienyl ligand and one to three heteroatom ligands, the balance of the transition metal coordination requirement being satisfied with cyclopentadienyl or hydrocarbyl ligands. Catalyst systems described by this reference are illustrated solely with reference to transition metal compounds which

are metallocenes, i.e., bis(cyclopentadienyl) Group IV B transition metal compounds.

Even more recently, at the Third Chemical Congress of North American held in Toronto, Canada in June 1988, John Bercaw reported upon efforts to use a compound of a Group III B transition metal coordinated to a single cyclopentadienyl heteroatom bridged ligand as a catalyst system for the polymerization of olefins. Although some catalytic activity was observed under the conditions employed, the degree of activity and the properties observed in the resulting polymer product were discouraging of a belief that such monocyclopentadienyl transition metal compound could be usefully employed for commercial polymerization processes.

A need still exists for discovering catalyst systems that permit the production of higher molecular weight polyolefins and desirably with a narrow molecular weight distribution. It is further desirable that a catalyst be discovered which will catalyze the polymerization of an  $\alpha$ -olefin monomer(s) to a highly crystalline form of poly- $\alpha$ -olefin i.e., the product polymer resin is free or substantially free of atactic stereochemical forms of poly- $\alpha$ -olefin molecules which are amorphous.

Polymers comprised of  $\alpha$ -olefin monomers have hydrocarbyl groups pendant from the polymer backbone chain. Relative to the polymer backbone chain, the pendant hydrocarbyl groups may be arranged in different stereochemical configurations which are denominated as, for example, atactic, isotactic, or syndiotactic pendant group configuration.

The degree and type of tacticity of a polyolefin molecule <sup>are</sup> ~~is a~~ critical determinant<sup>s</sup> of the physical properties which a resin composed of such polymer molecules will exhibit. Other critical determinants of the properties which a resin will exhibit are the type

and relative concentration of monomers and comonomers, the weight average molecular weight ( $M_w$ ) of the polymer molecules comprising the resin bulk, the molecular weight distribution (MWD) and the composition distribution of the resin.

Important from a commercial standpoint is the rate or productivity at which a catalyst system will produce a poly- $\alpha$ -olefin resin of a desired set of properties in terms of tacticity, weight average molecular weight and molecular weight distribution.

The weight average molecular weight ( $M_w$ ) of a poly- $\alpha$ -olefin is an important physical property determinant of the practical uses to which such polymer can be put. For end use applications which require high strength and low creep, the  $M_w$  of such a resin must generally be in excess of 100,000. Further, for such high strength applications, the poly- $\alpha$ -olefin resin must generally have a high degree of crystallinity. The degree of crystallinity which a poly- $\alpha$ -olefin is capable of obtaining is, in major part, determined by the stereochemical regularity of the hydrocarbyl groups which are pendent to the polymer molecule backbone, i.e., the tacticity of the polymer.

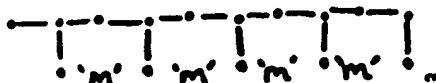
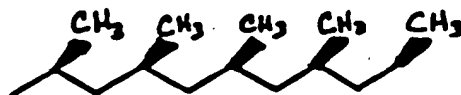
Five types of tacticity have been described in poly- $\alpha$ -olefins: atactic, normal isotactic, isotactic stereoblock, syndiotactic, and hemiisotactic. Although all of these tacticity configurations have been primarily demonstrated in the case of polypropylene, in theory each is equally possible for polymers comprised of any  $\alpha$ -olefin, cyclic olefin or internal olefin.

Atactic poly- $\alpha$ -olefins are those wherein the hydrocarbyl groups pendent to the polymer molecule backbone assume no regular order in space with reference to the backbone. This random, or atactic, structure is represented by a polymer backbone of alternating

methylene and methine carbons, with randomly oriented branches substituting the methine carbons. The methine carbons randomly have R and S configurations, creating adjacent pairs either of like configuration (a "meso" or "m" dyad) or of unlike configuration (a "racemic" or "r" dyad). The atactic form of a polymer contains approximately equal fractions of meso and racemic dyads.

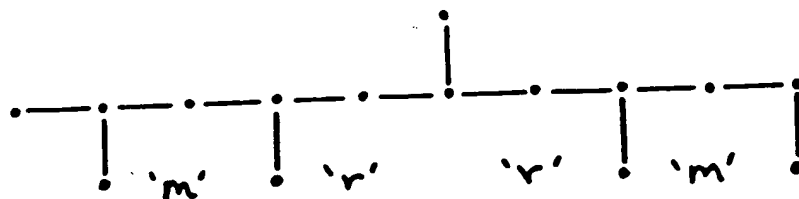
Atactic poly- $\alpha$ -olefins, particularly atactic polypropylene, are soluble in aliphatic and aromatic solvents at ambient temperature. Since atactic polymers exhibit no regular order or repeating unit configurations in the polymer chain, such atactic polymers are amorphous materials. Since atactic poly- $\alpha$ -olefins are amorphous, the resins composed thereof have no measurable melting point. Atactic polymers exhibit little if any crystallinity, hence they are generally unsuitable for high strength applications regardless of the weight average molecular weight of the resin.

Isotactic poly- $\alpha$ -olefins are those wherein the pendent hydrocarbyl groups are ordered in space to the same side or plane of the polymer backbone chain. Using isotactic polypropylene as an example, the isotactic structure is typically described as having the pendent methyl groups attached to the ternary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the carbon backbone chain of the polymer, e.g., the methyl groups are all above or below the plane as shown below.

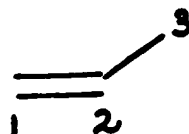
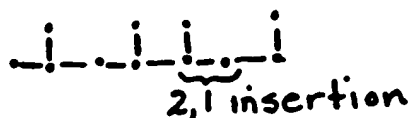
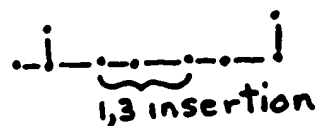


The degree of isotactic regularity may be measured by NMR techniques. Bovey's NMR nomenclature for an isotactic pentad is ... mmm ... with each "m" representing a "meso" dyad or successive methyl groups on the same side <sup>of</sup> in the plane.

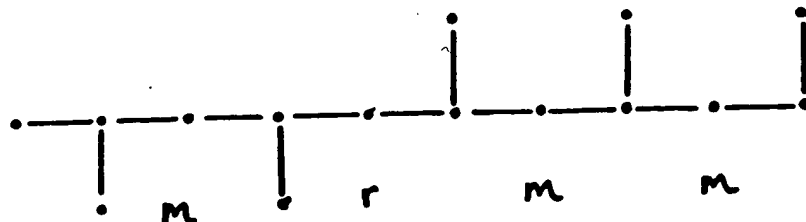
In the normal isotactic structure of a poly- $\alpha$ -olefin, all of the monomer units have the same stereochemical configuration, with the exception of random errors which appear along the polymer. Such random errors almost always appear as isolated inversions of configuration which are corrected in the very next  $\alpha$ -olefin monomer insertion to restore the original R or S configuration of the propagating polymer chain. Single insertions of inverted configuration give rise to rr triads, which distinguish this isotactic structure in its NMR from the isotactic stereoblock form.



As is known in the art, any deviation or inversion in the regularity of the structure of the chains lowers the degree of isotacticity and hence the crystallinity of which the polymer is capable. There are two other types of "errors" which have been observed in isotactic polymers prepared using metallocene-alumoxane catalyst systems which act to lower the melting point and/or  $T_g$  of the material. These errors, as shown below arise when a monomer is added to the growing polymer chain in a 1, 3 or 2, 1 fashion.



Long before anyone had discovered a catalyst system which produced the isotactic stereoblock form of a poly- $\alpha$ -olefin, the possible existence of a polymer of such micro-structure had been recognized and mechanisms for its formation had been proposed based on conventional Ziegler-Natta mechanisms in Langer, A.W., Lect. Bienn. Polym. Symp. 7th (1974); Ann. N.Y. Acad. Sci. 295, 110-126 (1977). The first example of this form of polypropylene and a catalyst which produces it in a pure form were reported in U.S. Patent No. 4,522,982. The formation of stereoblock isotactic polymer differs from the formation of the normal isotactic structure in the way that the propagation site reacts to a stereochemical error in the chain. As mentioned above, the normal isotactic chain will return to the original configuration following an error because the stereochemical regulator, the catalytic active metal species and its surrounding ligands, continue to dictate the same stereochemical preference during monomer insertion. In stereoblock propagation, the catalytic active metal site itself changes from one which dictates a monomer insertion of R configuration to one which dictates an S configuration for monomer insertion. The isotactic stereoblock form is shown below.



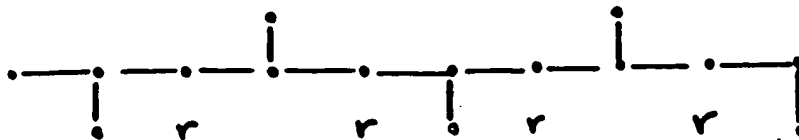


This occurs either because the metal and its ligands change to the opposite stereochemical configuration or because the configuration of the last added monomer, rather than the metal chirality, controls the configuration of the next added monomer. In Ziegler-Natta catalysts, including the above referenced system, the exact structure and dynamic properties of the active site are not well understood, and it is virtually impossible to distinguish between the "site chirality exchange" and "chain end control" mechanisms for the formation of isotactic stereoblock poly- $\alpha$ -olefins.

Unlike normal isotactic polymers, the lengths of individual blocks of the same configuration in the stereoblock structure vary widely due to changing reaction conditions. Since only the erroneous parts of the chains affect the crystallinity of the resin product, in general, normal isotactic polymers and isotactic stereoblock polymers of long block length (greater than 50 isotactic placements) have similar properties.

Highly isotactic poly- $\alpha$ -olefins are insoluble in xylene and are capable of exhibiting a high degree of crystallinity and are in part characterizable by their melting point temperature. Accordingly, isotactic poly- $\alpha$ -olefins are, depending upon their weight average molecular weight exceeding about 100,000, well suited to high strength end use applications.

Syndiotactic poly- $\alpha$ -olefins are those wherein the hydrocarbyl groups pendent to the polymer molecular backbone alternate sequentially in order from one side or plane to the opposite side or plane relative to the polymer backbone, as shown below.



In NMR nomenclature, this pentad is described as ... rrrr ... in which each r represents a "racemic" dyad, i.e., successive methyl groups on alternate sides of the plane. The percentage of r dyads in the chain determines the degree of syndiotacticity of the polymer.

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B  
Syndiotactic propagation has been studied for over 25 years; however, only a few good syndiospecific catalysts have been discovered, all of which are extremely sensitive to monomer bulkiness. As a result, well-characterized syndiotactic polymers are limited only to ~~polypropylenes~~. The molecular chain backbone of a syndiotactic polymer can be considered to be a copolymer of olefins with alternating stereochemical configurations. Highly syndiotactic polymers are generally highly crystalline and will frequently have high melting points similar to their isotactic polymorphs.

20 Like isotactic poly- $\alpha$ -olefins, syndiotactic poly- $\alpha$ -olefins are capable of exhibiting a high degree of crystallinity, hence are suitable for high strength applications provided their  $M_w$  exceeds about 100,000. Syndiotactic poly- $\alpha$ -olefins are in part characterized by their exhibition of a melting point temperature.

B  
B  
30 For any of the above described materials the final resin properties and <sup>their</sup> ~~its~~ suitability for particular applications depend <sup>S</sup> on the type of tacticity, the melting point (stereoregularity), the average molecular weight, the molecular weight distribution, the type and level of monomer and comonomer, the sequence distribution, and the presence or absence of head or end group functionality. Accordingly, the catalyst system by which such a stereoregular poly- $\alpha$ -olefin resin is to be produced should, desirably, be versatile in terms of  $M_w$ , MWD,

tacticity type and level, and comonomer choice. Further, the catalyst system should be capable of producing these polymers with or without head and/or end group functionality, such as olefinic unsaturation. Still further, such catalyst system must be capable, as a commercially practical constraint, of producing such resins at an acceptable production rate. Most preferably, the catalyst system should be one which, at its productivity rate, provides a resin product which does not require a subsequent treatment to remove catalyst residue to a level which is acceptable for the resin in the end use application desired. Finally, an important feature of a commercial catalyst system is its adaptability to a variety of processes and conditions.

Conventional titanium based Ziegler-Natta catalysts for the preparation of isotactic polymers are well known in the art. These commercial catalysts are well suited for the production of highly crystalline, high molecular weight materials. The systems are, however, limited in terms of molecular weight, molecular weight distribution, and tacticity control. The fact that the conventional catalysts contain several types of active sites further limits their ability to control the composition distribution in copolymerization.

More recently a new method of producing isotactic polymers from an alumoxane cocatalyzed, or activated, metallocene which in its natural state has chirality centered at the transition metal of the metallocene, was reported in Ewen, J.A., J. Amer. Chem. Soc., v. 106, p. 6355 (1984) and Kaminsky, W., et al., Angew. Chem. Int. Ed. Eng.; 24, 507-8 (1985).

Catalysts that produce isotactic polyolefins are also disclosed in Patent No. 4,794,096. This patent discloses a chiral, stereorigid metallocene catalyst which is activated by an alumoxane cocatalyst which is

reported to polymerize olefins to isotactic polyolefin forms. Alumoxane cocatalyzed metallocene structures which have been reported to polymerize stereoregularly are the ethylene bridged bis-indenyl and bis-tetrahydroindenyl titanium and zirconium (IV) catalyst. Such catalyst systems were synthesized and studied in Wild et al., J. Organomet. Chem. 232, 233-47 (1982), and were later reported in Ewen and Kaminsky et al., mentioned above, to polymerize  $\alpha$ -olefins stereoregularly. Further reported in West German Off DE 3443087A1 (1986), but without giving experimental verification, is that the bridge length of such stereorigid metallocenes can vary from a C<sub>1</sub> to C<sub>4</sub> hydrocarbon and the metallocene rings can be simple or bi-cyclic but must be asymmetric.

Metallocene-alumoxane catalyst generally require a high content of alumoxane cocatalyst to be sufficiently productive for commercial use. Accordingly, metallocene-alumoxane produced isotactic poly- $\alpha$ -olefin resins generally have a higher than desired catalyst residue content. Hafnocene systems, which yield polymers of higher average  $M_w$  than the zirconium analogs, have very low activities even at high alumoxane concentrations.

Syndiotactic polyolefins were first disclosed by Natta et al. in U.S. Patent No. 3,258,455. As reported, Natta obtained syndiotactic polypropylene by using a catalyst prepared from titanium trichloride and diethyl aluminum monochloride. A later patent to Natta et al., U.S. Patent No. 3,305,538, discloses the use of vanadium triacetylacetonate or halogenated vanadium compounds in combinations with organic aluminum compounds for production of syndiotactic polypropylene.

More recently, a metallocene based catalyst system has been disclosed which is stated to be capable of production of syndiotactic polypropylene of high stereoregularity. U S. Patent No. 4,892,851 describes.

catalyst systems consisting of a bridged metallocene having at least two differently substituted cyclopentadienyl ring ligands which, when cocatalyzed with an alumoxane, is stated to be capable of production of syndiotactic polypropylene. Again, in commercial production to obtain a sufficient productivity level with such catalyst system, the content of alumoxane is undesirably high and consequently the catalyst residue in the resin so produced is undesirably high.

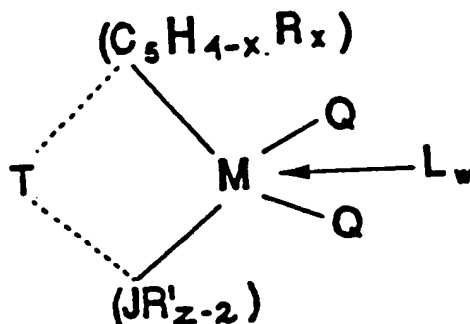
In all methylalumoxane/metallocene catalyst systems the polymer characteristics ( $M_w$ , MWD, tacticity type, comonomer incorporation, etc.) are controlled either by modifications to the structure of the metallocene precursor or by adjustment of the process conditions (temperature, pressure, concentrations). In general, adjustment of process conditions does not allow independent control of tacticity level,  $M_w$  and comonomer content. Addition of chain transfer agents such as hydrogen gas to the reactor gives lower molecular weight products without affecting tacticity, however, the resulting polymer no longer has unsaturated end groups. End group functionalization is often an important feature in the application of low molecular weight polymers. Given these limitations, one must prepare a wide variety of differently substituted metallocene precursors to access the entire range of desired materials.

In view of the difficulty and practical limitations in the synthesis of bridged metallocene complexes necessary for the production of an alumoxane activated metallocene catalyst system capable of producing crystalline poly- $\alpha$ -olefins, it would be desirable to develop new catalytic processes which produce highly crystalline forms of poly- $\alpha$ -olefins of high molecular weight and relatively narrow molecular weight distributions.

# SUMMARY OF THE INVENTION

The process of this invention employs a catalyst system comprised of a transition metal component from Group IV B of the Periodic Table of the Elements (CRC Handbook of Chemistry and Physics, 68th ed. 1987-1988) and an alumoxane component. The catalyst system may be employed in solution, slurry, <sup>gas</sup> or bulk phase polymerization procedure to produce crystalline poly- $\alpha$ -olefins of high weight average molecular weight and relatively narrow molecular weight distribution.

The "Group IV B transition metal component" of the catalyst system is represented by the formula:



wherein: M is Zr, Hf or Ti in its highest formal oxidation state (+4,  $d^0$  complex);

$(C_5H_{4-x}R_x)$  is a cyclopentadienyl ring which is substituted with from zero to four substituent groups R, "x" is 0, 1, 2, 3, or 4 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of  $C_1$ - $C_{20}$  hydrocarbyl radicals, substituted  $C_1$ - $C_{20}$  hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality,  $C_1$ - $C_{20}$  hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; and halogen radicals, amido radicals,

B phosphido radicals, alkoxy radicals, alkylborido radicals or any other radical containing <sup>α</sup> Lewis acidic or basic functionality; or  $(C_5H_4-xR_x)$  is a cyclopentadienyl ring in which at least two adjacent R-groups are joined forming a  $C_4-C_{20}$  ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl,

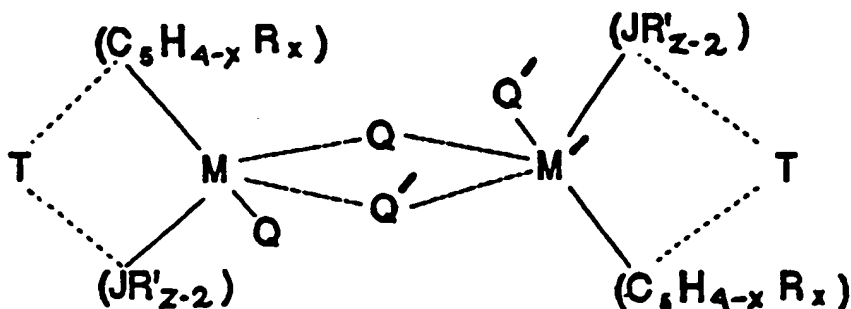
(JR'<sub>z-2</sub>) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VI A of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur, and each R' is, independently a radical selected from a group consisting of  $C_1-C_{20}$  hydrocarbyl radicals, substituted  $C_1-C_{20}$  hydrocarbyl radicals wherein one or more hydrogen atoms are replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality, and "z" is the coordination number of the element J;

B each Q may be independently any univalent anionic ligand such as a halide, hydride, or substituted or unsubstituted  $C_1-C_{20}$  hydrocarbyl, alkoxide, aryloxide, amide, arylamide, phosphide or arylphosphide, provided that where any Q is a hydrocarbyl such Q is different from  $(C_5H_4-xR_x)$ , or both Q together may be an alkylidene or a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand;

30 T is a covalent bridging group containing a Group IV A or V A element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like;

35 L is a neutral Lewis base such as diethylether, tetraethylammonium chloride, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-

butylamine, and the like; and "w" is a number from 0 to 3. L can also be a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q. Such dimeric compounds are represented by the formula:



The alumoxane component of the catalyst may be represented by the formulas: (R<sup>3</sup>-Al-O)<sub>m</sub>; R<sup>4</sup>(R<sup>5</sup>-Al-O)<sub>m</sub><sup>-</sup>AlR<sub>2</sub><sup>6</sup> or mixtures thereof, wherein R<sup>3</sup>-R<sup>6</sup> are, independently, a C<sub>1</sub>-C<sub>5</sub> alkyl group or halide and "m" is an integer ranging from 1 to about 50 and preferably is from about 13 to about 25.

Catalyst systems of the invention may be prepared by placing the "Group IV B transition metal component" and the alumoxane component in common solution in a normally liquid alkane or aromatic solvent, which solvent is preferably suitable for use as a polymerization diluent for the liquid phase polymerization of an α-olefin monomer.

Those species of the Group IV B transition metal component wherein the metal is titanium have been found to impart beneficial properties to a catalyst system which are unexpected in view of what is known about the properties of bis(cyclopentadienyl) titanium compounds which are cocatalyzed by alumoxanes. Whereas titanocenes



in their soluble form are generally unstable in the presence of aluminum alkyls, the monocyclopentadienyl titanium metal components of this invention, particularly those wherein the heteroatom is nitrogen, generally exhibit greater stability in the presence of aluminum alkyls and higher catalyst activity rates.

Further, the titanium species of the Group IV B transition metal component catalyst of this invention generally exhibit higher catalyst activities and the production of poly- $\alpha$ -olefins of greater molecular weight than catalyst systems prepared with the zirconium or hafnium species of the Group IV B transition metal component.

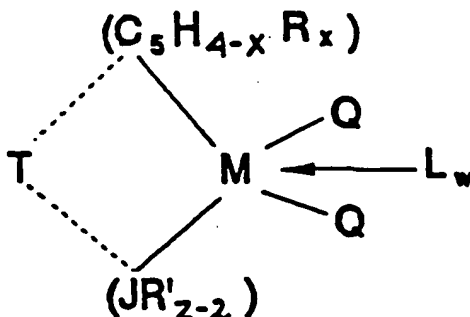
A typical polymerization process of the invention such as for the polymerization or copolymerization of propylene comprises the steps of contacting propylene or other  $C_4$ - $C_{20}$   $\alpha$ -olefins alone, or with other unsaturated monomers including  $C_3$ - $C_{20}$   $\alpha$ -olefins,  $C_5$ - $C_{20}$  diolefins, and/or acetylenically unsaturated monomers either alone or in combination with other olefins and/or other unsaturated monomers, with a catalyst comprising, in a suitable polymerization diluent, a Group IV B transition metal component illustrated above; and a methylalumoxane in an amount to provide a molar aluminum to transition metal ratio of from about 1:1 to about 20,000:1 or more; and reacting such monomer in the presence of such catalyst system at a temperature of from about  $-100^\circ\text{C}$  to about  $300^\circ\text{C}$  for a time of from about 1 second to about 10 hours to produce a poly- $\alpha$ -olefin having a weight average molecular weight of from about 1,000 or less to about 2,000,000 or more and a molecular weight distribution of from about 1.5 to about 15.0.

As discussed further hereafter, by proper selection of the type and pattern R substituents for the cyclopentadienyl ligand in relationship to the type of R' substituent of the heteroatom ligand the transition metal component for the catalyst system may be tailored to function in the catalyst system to produce highly crystalline poly- $\alpha$ -olefins to the total or substantial avoidance of the production of atactic poly- $\alpha$ -olefin molecules which are amorphous.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

##### Catalyst Component

The Group IV B transition metal component of the catalyst system is represented by the general formula:



wherein M is Zr, Hf or Ti in its highest formal oxidation state (+4,  $d^0$  complex);

$(\text{C}_5\text{H}_{4-x}\text{R}_x)$  is a cyclopentadienyl ring which is substituted with from zero to four substituent groups R, "x" is 0, 1, 2, 3, or 4 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of  $\text{C}_1$ - $\text{C}_{20}$  hydrocarbyl radicals, substituted  $\text{C}_1$ - $\text{C}_{20}$  hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, and alkoxy radical or any other

radical containing a Lewis acidic or basic functionality,  
C<sub>1</sub>-C<sub>20</sub> hydrocarbyl-substituted metalloid radicals wherein  
the metalloid is selected from the Group IV A of the  
Periodic Table of Elements; and halogen radicals, amido  
5 radicals, phosphido radicals, alkoxy radicals,  
alkylborido radicals or any other radical containing  
Lewis acidic or basic functionality; or (C<sub>5</sub>H<sub>4-x</sub>R<sub>x</sub>) is a  
cyclopentadienyl ring in which two adjacent R-groups are  
joined forming C<sub>4</sub>-C<sub>20</sub> ring to give a saturated or  
10 unsaturated polycyclic cyclopentadienyl ligand such as  
indenyl, tetrahydroindenyl, fluorenyl or  
octahydrofluorenyl;

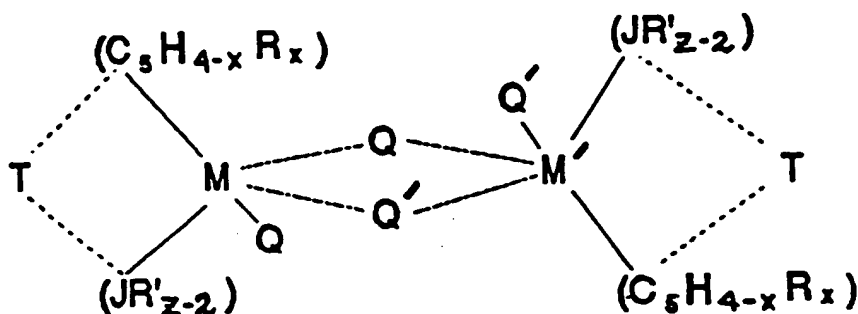
(JR'<sub>z-2</sub>) is a heteroatom ligand in which J is an  
element with a coordination number of three from Group V  
15 A or an element with a coordination number of two from  
Group VI A of the Periodic Table of Elements, preferably  
nitrogen, phosphorus, oxygen or sulfur with nitrogen  
being preferred, and each R' is, independently a radical  
selected from a group consisting of C<sub>1</sub>-C<sub>20</sub> hydrocarbyl  
20 radicals, substituted C<sub>1</sub>-C<sub>20</sub> hydrocarbyl radicals wherein  
one or more hydrogen atoms is replaced by a halogen  
radical, an amido radical, a phosphido radical, an alkoxy  
radical or any other radical containing a Lewis acidic or  
basic functionality, and "z" is the coordination number  
25 of the element J;

each Q is, independently, any univalent anionic  
ligand such as a halide, hydride, or substituted or  
unsubstituted C<sub>1</sub>-C<sub>20</sub> hydrocarbyl, alkoxide, aryloxide,  
amide, arylamide, phosphide or arylphosphide, provided  
30 that where any Q is a hydrocarbyl such Q is different  
from (C<sub>5</sub>H<sub>4-x</sub>R<sub>x</sub>), or both Q together may be an alkylidene  
or a cyclometallated hydrocarbyl or any other divalent  
anionic chelating ligand;

T is a covalent bridging group containing a Group IV  
35 A or V A element such as, but not limited to, a dialkyl,

alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like;

and L is a neutral Lewis base such as diethylether, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and "w" is a number from 0 to 3; L can also be a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q. Such compounds are represented by the formula:



Examples of the T group which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in column 1 of Table 1 under the heading "T".

Suitable, but not limiting, Group IV B transition metal compounds which may be utilized in the catalyst system of this invention include those wherein the T group bridge is a dialkyl, diaryl or alkylaryl silane, or methylene or ethylene. Exemplary of the more preferred species of bridged Group IV B transition metal compounds are dimethylsilyl, methylphenylsilyl, diethylsilyl, ethylphenylsilyl, diphenylsilyl, ethylene or methylene bridged compounds. Most preferred of the bridged species are dimethylsilyl, diethylsilyl and methylphenylsilyl bridged compounds.

Exemplary hydrocarbyl radicals for Q are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like, with methyl being preferred. Exemplary halogen atoms for Q include chlorine, bromine, fluorine and iodine, with chlorine being preferred. Exemplary alkoxides and aryloxides for Q are methoxide, phenoxide and substituted phenoxides such as 4-methylphenoxide. Exemplary amides of Q are dimethylamide, diethylamide, methylethylamide, di-~~t~~<sup>p</sup>-butylamide, diisopropylamide and the like. Exemplary aryl amides are diphenylamide and any other substituted phenyl amides. Exemplary phosphides of Q are diphenylphosphide, dicyclohexylphosphide, diethylphosphide, dimethylphosphide and the like. Exemplary alkyldiene radicals for both Q together are methyldiene, ethyldiene and propyldiene. Examples of the Q group which are suitable as a constituent group or element of the Group IV B transition metal component of the catalyst system are identified in column 4 of Table 1 under the heading "Q".

Suitable hydrocarbyl and substituted hydrocarbyl radicals, which may be substituted as an R group for at least one hydrogen atom in the cyclopentadienyl ring, will contain from 1 to about 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals, amido-substituted hydrocarbon radicals, phosphido-substituted hydrocarbon radicals, alkoxy-substituted hydrocarbon radicals, and cyclopentadienyl rings containing one or more fused saturated or unsaturated rings. Suitable organometallic radicals, which may be substituted as an R group for at least one hydrogen atom in the cyclopentadienyl ring, include

trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, trimethylgermyl and the like. Other suitable radicals that may be substituted for one or more hydrogen atom in the cyclopentadienyl ring include halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkylborido radicals and the like. Examples of cyclopentadienyl ring groups ( $C_5H_{4-x}R_x$ ) which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in column 2 of Table 1 under the heading ( $C_5H_{4-x}R_x$ ).

Suitable hydrocarbyl and substituted hydrocarbyl radicals, which may be substituted as an  $R'$  group for at least one hydrogen atom in the heteroatom J ligand group, will contain from 1 to about 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radical, halogen radicals, amido radicals, phosphido radicals and the like. Examples of heteroatom ligand groups ( $JR'_{2-2}$ ) which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in column 3 of Table 1 under the heading ( $JR'_{2-2}$ ).

Table 1 depicts representative constituent moieties for the "Group IV B transition metal component", the list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting all possible combinations of the constituent moieties with each other. Illustrative compounds are: dimethylsilylfluorenyl-t-butylamido zirconium dichloride, dimethylsilylfluorenyl-t-butylamido hafnium dichloride, dimethylsilylfluorenylhexylamidozirconiumdihalides.

and dimethylsilylfluorenylcyclohexylamido hafnium dichloride.

As noted, titanium species of the Group IV B transition metal compound have generally been found to yield catalyst systems which in comparison to their zirconium or hafnium analogues, are of higher activity. Illustrative, but not limiting of the titanium species which may exhibit such superior properties are dimethylsilylfluorenyl-t-butylamido titanium dichloride, dimethylsilylindenylcyclohexylamido titanium dichloride, dimethylsilyl-t-butylcyclopentadienylcyclododecylamido titanium dichloride, dimethylsilylmethylcyclopentadienylcyclododecylamido titanium dichloride, dimethylsilylmethylcyclopentadienyl-2,6-diisopropylphenylamido titanium dichloride, dimethylsilylmethylcyclopentadienylcyclohexylamido titanium dichloride, and dimethylsilylmethylcyclopentadienyl-2,5-di-t-butylphenylamido titanium dichloride.

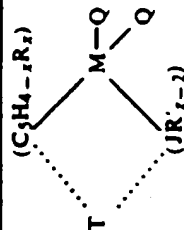
For illustrative purposes, the above compounds and those permuted from Table 1 do not include the neutral Lewis base ligand (L). The conditions under which complexes containing neutral Lewis base ligands such as ether or those which form dimeric compounds are determined by the steric bulk of the ligands about the metal center. For example, the t-butyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$  has greater steric requirements than the phenyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NPh})\text{ZrCl}_2 \cdot \text{Et}_2\text{O}$  thereby not permitting ether coordination in the former compound. Similarly, due to the decreased steric bulk of the trimethylsilylcyclopentadienyl group in  $[\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-t-Bu})\text{ZrCl}_2]_2$  versus that of the tetramethylcyclopentadienyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$

b Bu)ZrCl<sub>2</sub>, the former compound is dimeric and the latter is not.

5 To illustrate members of the Group IV B transition metal component, select any combination of the species in Table 1. An example of a bridged species would be  
b dinethylsilylcyclopentadienyl-<sup>1/2</sup>t-butylamidodichloro zirconium.



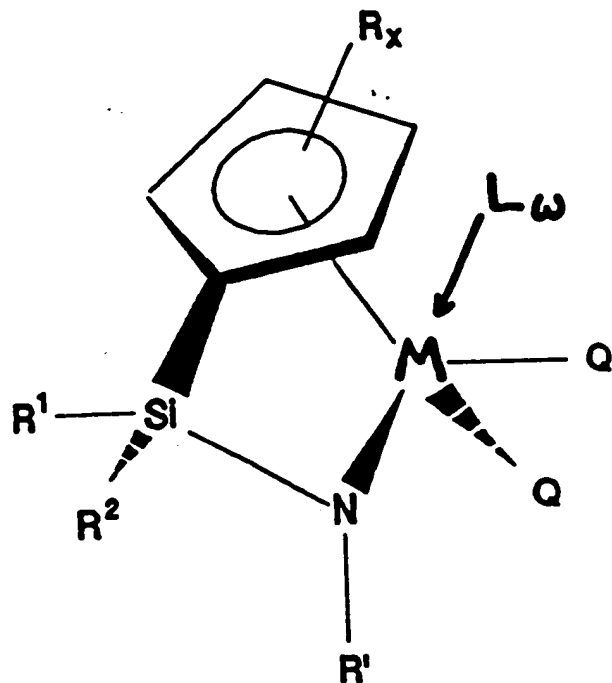
TABLE I



T	$(C_3H_4 - xR_z)$	$(JR' - 2)$	Q	M
dimethylsilyl	cyclopentadienyl	i-butylamido	hydride	zirconium
diethylsilyl	methylcyclopentadienyl	phenylamido	chloro	hafnium
di-n-propylsilyl	1,2-dimethylcyclopentadienyl	p-n-butylphenylamido	methyl	titanium
diisopropylsilyl	1,3-dimethylcyclopentadienyl	cyclohexylamido	ethyl	
di-n-butylsilyl	indenyl	perfluorophenylamido	phenyl	
di-t-butylsilyl	1,2-diethylcyclopentadienyl	n-butylamido	fluoro	
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	bromo	
methylphenylsilyl	ethylcyclopentadienyl	ethylamido	iodo	
ethylmethylsilyl	n-butylcyclopentadienyl	n-propylamido	n-propyl	
diphenylsilyl	cyclohexylmethylcyclopentadienyl	isopropylamido	isopropyl	
di(p-t-butylphenethylsilyl)	n-octylcyclopentadienyl	benzylamido	n-butyl	
n-hexylmethylsilyl	$\beta$ -phenylpropylcyclopentadienyl	i-butylphosphido	amyl	
cyclopentamethylenesilyl	tetrahydroindenyl	ethylphosphido	isoamyl	
cyclotetramethylenesilyl	propylcyclopentadienyl	phenylphosphido	heptyl	
cyclotrimethylenesilyl	t-butylcyclopentadienyl	cyclohexylphosphido	isobutyl	
dimethylgermanyl	benzylcyclopentadienyl	oxo	heptyl	
diethylgermanyl	diphenylmethylcyclopentadienyl	sulfido	octyl	
phenylamido	trimethylgermylcyclopentadienyl		nonyl	
i-butylamido	trimethylstannylcyclopentadienyl		decyl	
methylamido	triethylplumbylcyclopentadienyl		cetyl	
i-butylphosphido	triisobutylmethylcyclopentadienyl		methoxy	
ethylphosphido	trimethylsilylcyclopentadienyl		ethoxy	
phenylphosphido	fluorenyl		propoxy	
methylene	octahydrofluorenyl		butoxy	
diethylmethylene	N,N-dimethylamidocyclopentadienyl		phenoxy	
ethylene	dimethylphosphidocyclopentadienyl		dimethylamido	
dimethylethylene	methoxycyclopentadienyl		diethylamido	
diethylethylene	dimethylboridocyclopentadienyl		methylethylamido	
dipropylethylene	(N,N-dimethylamidomethyl)cyclopentadienyl		di-t-butylamido	
propylene	tetrafluorocyclopentadienyl		diphenylamido	
dimethylpropylene			diphenylphosphido	
diethylpropylene			dicyclohexylphosphido	
1,1-dimethyl-3,3-dimethylpropylene			dimethylphosphido	
tetramethyldisiloxane			methylidene (both Q)	
1,1,4,4-tetramethyldisilylethylene			ethylidene (both Q)	
			propylidene (both Q)	

B  
B  
5 The Group IV B transition metal compounds can be prepared by reacting a cyclopentadienyl lithium compound with a dihalo compound, whereupon a lithium halide salt is liberated and a monohalo substituent becomes covalently bound to the cyclopentadienyl compound. The so substituted cyclopentadienyl reaction product is next reacted with a lithium salt of a phosphide, oxide, sulfide or amide (for the sake of illustrative purposes, a lithium amide) whereupon the halo element of the  
10 monohalo substituent group of the reaction product reacts to liberate a lithium halide salt and the amine moiety of the lithium amide salt becomes covalently bound to the substituent of the cyclopentadienyl reaction product. The resulting amine derivative of the cyclopentadienyl  
15 product is then reacted with an alkyl lithium reagent whereupon the labile hydrogen atoms, at the carbon atom of the cyclopentadienyl compound and at the nitrogen atom of the amine moiety covalently bound to the substituent group, react with the alkyl of the lithium alkyl reagent  
20 to liberate the alkane and produce a dilithium salt of the cyclopentadienyl compound. Thereafter the bridged species of the Group IV B transition metal compound is produced by reacting the dilithium salt cyclopentadienyl compound with a Group IV B transition metal preferably a  
25 Group IV B transition metal halide.

B  
30 The class of transition metal components most preferred for use in the process for production of crystalline poly- $\alpha$ -olefins is that wherein the covalent bridging group T contains silicon and the heteroatom J of the heteroatom ligand is nitrogen. Accordingly, the preferred class of transition metal components are of the formula:



wherein Q, L, R<sup>1</sup>, R, "x" and "w" are as previously defined and R<sup>1</sup> and R<sup>2</sup> are each independently a C<sub>1</sub> to C<sub>20</sub> hydrocarbyl radicals, substituted C<sub>1</sub> to C<sub>20</sub> hydrocarbyl radicals wherein one or more hydrogen atom is replaced by a halogen atom; R<sup>1</sup> and R<sup>2</sup> may also be joined forming a C<sub>3</sub> to C<sub>20</sub> ring which incorporates the silicon bridge.

The alumoxane component of the catalyst system is an oligomeric compound which may be represented by the general formula (R<sup>3</sup>-Al-O)<sub>m</sub> which is a cyclic compound, or may be R<sup>4</sup>(R<sup>5</sup>-Al-O)<sub>m</sub>-AlR<sup>6</sup><sub>2</sub> which is a linear compound. An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are, independently a C<sub>1</sub>-C<sub>5</sub> alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "m" is an integer from 1 to about 50. Most preferably, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are each methyl and "m" is at least 4. When an alkyl aluminum halide is employed in

the preparation of the alumoxane, one or more  $R^{3-6}$  groups may be halide.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of a trialkyl aluminum with a limited amount of water yields a mixture of both linear and cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the catalyst systems of this invention are those prepared by the hydrolysis of a trialkylaluminum; such as trimethylaluminum, triethylaluminum, tripropylaluminum; triisobutylaluminum, dimethylaluminumchloride, diisobutylaluminumchloride, diethylaluminumchloride, and the like. The most preferred alumoxane for use is methylalumoxane (MAO). Methylalumoxanes having an average degree of oligomerization of from about 4 to about 25 ("m" = 4 to 25), with a range of 13 to 25, are the most preferred.

#### Catalyst Systems

The catalyst systems employed in the method of the invention comprise a complex formed upon admixture of the Group IV B transition metal component with an alumoxane component. The catalyst system may be prepared by addition of the requisite Group IV B transition metal and alumoxane components to an inert solvent in which olefin polymerization can be carried out by a solution, slurry, or bulk phase polymerization procedure.

The catalyst system may be conveniently prepared by placing the selected Group IV B transition metal component and the selected alumoxane component in any

B order of addition, in an alkane or aromatic hydrocarbon solvent -- preferably one which is also suitable for service as a polymerization diluent. <sup>When</sup> ~~where~~ the hydrocarbon solvent utilized is also suitable for use as a polymerization diluent, the catalyst system may be prepared in situ in the polymerization reactor. Alternatively, the catalyst system may be separately prepared, in concentrated form, and added to the polymerization diluent in a reactor. <sup>If</sup> ~~Or, if~~ desired, the components of the catalyst system may be prepared as separate solutions and added to the polymerization diluent in a reactor, in appropriate ratios, as is suitable for a continuous liquid phase polymerization reaction procedure. Alkane and aromatic hydrocarbons suitable as solvents for formation of the catalyst system and also as a polymerization diluent are exemplified by, but are not necessarily limited to, straight and branched chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane and the like, cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and the like, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene and the like.

In accordance with this invention optimum results are generally obtained wherein the Group IV B transition metal compound is present in the polymerization diluent in a concentration of from about 0.0001 to about 1.0 millimoles/liter of diluent and the alumoxane component is present in an amount to provide a molar aluminum to transition metal ratio of from about 1:1 to about 20,000:1. Sufficient solvent should be employed so as to

provide adequate heat transfer away from the catalyst components during reaction and to permit good mixing.

5 The catalyst system ingredients -- that is, the Group IV B transition metal, the alumoxane, and polymerization diluent -- can be added to the reaction vessel rapidly or slowly. The temperature maintained during the contact of the catalyst components can vary widely, such as, for example, from -10° to 300°C. Greater or lesser temperatures can also be employed. Preferably, 10 during formation of the catalyst system, the reaction is maintained within a temperature of from about 25° to 100°C, most preferably about 25°C.

At all times, the individual catalyst system components, as well as the catalyst system once formed, 15 are protected from oxygen and moisture. Therefore, the reactions to prepare the catalyst system are performed in an oxygen and moisture free atmosphere and, where the catalyst system is recovered separately, it is recovered in an oxygen and moisture free atmosphere. Preferably, 20 therefore, the reactions are performed in the presence of an inert dry gas such as, for example, helium or nitrogen.

#### Polymerization Process

B 25 In a preferred embodiment of the process of this invention, the catalyst system is utilized in the liquid phase (slurry, solution, suspension or bulk phase or combination thereof), high pressure fluid phase or gas phase polymerization of an  $\alpha$ -olefin monomer. These processes may be employed singularly or in series. The 30 liquid phase process comprises the steps of contacting an  $\alpha$ -olefin monomer with the catalyst system in a suitable polymerization diluent and reacting said monomer in the presence of said catalyst system for a time and at a temperature sufficient to produce a poly- $\alpha$ -olefin of high 35 crystallinity and molecular weight.

The monomer for such process comprises an  $\alpha$ -olefin having 3 to 20 carbon atoms. Propylene is a preferred monomer. Homopolymers of higher  $\alpha$ -olefin such as butene, styrene and copolymers thereof with ethylene and/or  $C_4$  or higher  $\alpha$ -olefins, diolefins, cyclic olefins and internal olefins can also be prepared. Conditions most preferred for the homo- or copolymerization of the  $\alpha$ -olefin are those wherein an  $\alpha$ -olefin is submitted to the reaction zone at pressures of from about 0.019 psia to about 50,000 psia and the reaction temperature is maintained at from about  $-100^\circ$  to about  $300^\circ C$ . The aluminum to transition metal molar ratio is preferably from about 1:1 to 18,000:1. A more preferable range would be 1:1 to 2000:1. The reaction time is preferably from about 10 seconds to about 1 hour. Without limiting in any way the scope of the invention, one means for carrying out the process of the present invention for production of a copolymer is as follows: in a stirred-tank reactor liquid  $\alpha$ -olefin monomer is introduced, such as propylene. The catalyst system is introduced via nozzles in either the vapor or liquid phase. The reactor contains a liquid phase composed substantially of the liquid  $\alpha$ -olefin monomer together with a vapor phase containing vapors of the monomer. The reactor temperature and pressure may be controlled via reflux of vaporizing  $\alpha$ -olefin monomer (autorefrigeration), as well as by cooling coils, jackets etc. The polymerization rate is controlled by the concentration of catalyst.

By appropriate selection of (1) Group IV B transition metal component for use in the catalyst system; (2) the type and amount of alumoxane used; (3) the polymerization diluent type and volume; (4) reaction temperature; and (5) reaction pressure, one may tailor the product polymer to the weight average molecular weight value desired while still maintaining the

molecular weight distribution to a value below about 4.0.

The preferred polymerization diluents for practice of the process of the invention are aromatic diluents, such as toluene, or alkanes, such as hexane.

5       The resins that are prepared in accordance with this invention can be used to make a variety of products including films and fibers.

#### EXAMPLES

10       In the examples which illustrate the practice of the invention the analytical techniques described below were employed for the analysis of the resulting polyolefin products. Molecular weight determinations for polyolefin products were made by Gel Permeation Chromatography (GPC) according to the following technique. Molecular weights  
15       and molecular weight distributions were measured using a Waters 150 gel permeation chromatograph equipped with a differential refractive index (DRI) detector and a Chromatix KMX-6 on-line light scattering photometer. The system was used at 135°C with 1,2,4-trichlorobenzene as  
20       the mobile phase. Shodex (Showa Denko America, Inc.) polystyrene gel columns 802, 803, 804 and 805 were used. This technique is discussed in "Liquid Chromatography of Polymers and Related Materials III", J. Cazes editor, Marcel Dekker. 1981, p. 207, which is incorporated herein  
25       by reference. No corrections for column spreading were employed; however, data on generally accepted standards, e.g. National Bureau of Standards Polyethylene 1484 and anionically produced hydrogenated polyisoprenes (an alternating ethylene-propylene copolymer) demonstrated  
30       that such corrections on Mw/Mn (= MWD) were less than 0.05 units. Mw/Mn was calculated from elution times. The numerical analyses were performed using the commercially available Beckman/CIS customized LALLS software in conjunction with the standard Gel Permeation package, run  
35       on a HP 1000 computer.



B Calculations involved in the characterization of polymers by <sup>13</sup>C NMR follow the work of F. A. Bovey in "Polymer Conformation and Configuration" Academic Press, New York, 1969.

5 The following examples are intended to illustrate specific embodiments of the invention and are not intended to limit the scope of the invention.

10 All procedures were performed under an inert atmosphere of helium or nitrogen. Solvent choices are often optional, for example, in most cases either pentane or 30-60 petroleum ether can be interchanged. The lithiated amides were prepared from the corresponding amines and either n-BuLi or MeLi. Published methods for preparing LiHC<sub>5</sub>Me<sub>4</sub> include C.M. Fendrick et al. 15 Organometallics, 3, 819 (1984) and F.H. Köhler and K. H. Doll, Z. Naturforsch., 37b, 144 (1982). Other lithiated substituted cyclopentadienyl compounds are typically prepared from the corresponding cyclopentadienyl ligand and n-BuLi or MeLi, or by reaction of MeLi with the 20 proper fulvene. TiCl<sub>4</sub>, ZrCl<sub>4</sub> and HfCl<sub>4</sub> were purchased from either Aldrich Chemical Company or Cerac. TiCl<sub>4</sub> was typically used in its etherate form. The etherate, TiCl<sub>4</sub>•2Et<sub>2</sub>O, can be prepared by gingerly adding TiCl<sub>4</sub> to diethylether. Amines, silanes and lithium reagents were 25 purchased from Aldrich Chemical Company or Petrarch Systems. Methylalumoxane was supplied by either Schering or Ethyl Corp.

Examples of Group IV B

Transition Metal - Components

Example A

30 Compound A: Part 1. Me<sub>2</sub>SiCl<sub>2</sub> (7.5 ml, 0.062 mol) was diluted with -30 ml of thf. A t-BuH<sub>4</sub>C<sub>5</sub>Li solution (7.29 g, 0.057 mol, -100 ml of <sup>THF</sup>thf) was slowly added, and the resulting mixture was allowed to stir overnight. The 35 thf was removed in vacuo. Pentane was added to

precipitate the LiCl, and the mixture was filtered through Celite. The pentane was removed from the filtrate leaving behind a pale yellow liquid,  $\text{Me}_2\text{Si}(\text{t-BuC}_5\text{H}_4)\text{Cl}$  (10.4 g, 0.048 mol).

5           Part 2.  $\text{Me}_2\text{Si}(\text{t-BuC}_5\text{H}_4)\text{Cl}$  (8.0 g, 0.037 mol) was  
diluted with <sup>THF</sup> ~~eth.~~. To this,  $\text{LiHNC}_{12}\text{H}_{23}$  (7.0 g, 0.037 mol)  
was slowly added. The mixture was allowed to stir  
overnight. The solvent was removed via vacuum and  
toluene was added to precipitate the LiCl. The toluene  
10 was removed from the filtrate leaving behind a pale  
yellow liquid,  $\text{Me}_2\text{Si}(\text{t-BuC}_5\text{H}_4)(\text{HNC}_{12}\text{H}_{23})$  (12.7 g, 0.035  
mol).

15           Part 3.  $\text{Me}_2\text{Si}(\text{t-BuC}_5\text{H}_4)(\text{HNC}_{12}\text{H}_{23})$  (12.7 g, 0.035 mol)  
was diluted with ether. To this, MeLi (1.4 M in ether,  
50 ml, 0.070 mol) was slowly added. This was allowed to  
stir for two hours prior to removing the solvent via  
vacuum. The product,  $\text{Li}_2[\text{Me}_2\text{Si}(\text{t-BuC}_5\text{H}_3)(\text{NC}_{12}\text{H}_{23})]$  (11.1  
g, 0.030 mol) was isolated.

20           Part 4.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{t-BuC}_5\text{H}_3)(\text{NC}_{12}\text{H}_{23})]$  (10.9 g, 0.029  
mol) was suspended in cold ether.  $\text{TiCl}_4 \cdot 2\text{Et}_2\text{O}$  (9.9 g,  
0.029 mol) was slowly added and the mixture was allowed  
to stir overnight. The solvent was removed via vacuum.  
Dichloromethane was added and the mixture was filtered  
through Celite. The solvent was removed<sup>d</sup> and pentane was  
25 added. The product is completely soluble in pentane.  
This solution was passed through a column containing a  
top layer of silica and a bottom layer of Celite. The  
filtrate was then evaporated down to an olive green  
colored solid identified as  $\text{Me}_2\text{Si}(\text{t-BuC}_5\text{H}_3)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$   
30 (5.27 g, 0.011 mol).

#### Example B

35           Compound B: Part 1.  $\text{Me}_2\text{SiCl}_2$  (210 ml, 1.25 mol)  
was diluted with a mixture of ether and <sup>THF</sup> ~~eth.~~.  $\text{LiMeC}_5\text{H}_4$   
(25 g, 0.29 mol) was slowly added, and the resulting  
mixture was allowed to stir for a few hours, after which

time the solvent was removed in vacuo. Pentane was added to precipitate the LiCl, and the mixture was filtered through Celite. The pentane was removed from the filtrate leaving behind a pale yellow liquid,  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)\text{Cl}$ .

Part 2.  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)\text{Cl}$  (10.0 g, 0.058 mol) was diluted with a mixture of ether and <sup>THF</sup>~~THF~~. To this,  $\text{LiHNC}_{12}\text{H}_{23}$  (11.0 g, 0.058 mol) was slowly added. The mixture was allowed to stir overnight. The solvent was removed via vacuum and toluene and pentane were added to precipitate the LiCl. The solvent was removed from the filtrate leaving behind a pale yellow liquid,  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HNC}_{12}\text{H}_{23})$  (18.4 g, 0.058 mol).

Part 3.  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HNC}_{12}\text{H}_{23})$  (18.4 g, 0.058 mol) was diluted in ether. MeLi (1.4 M in ether, 82 ml, 0.115 mol) was slowly added. The reaction was <sup>stirred</sup>~~allowed to stir~~ for several hours before reducing the ~~mixture in~~ volume and then filtering off the white solid,  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{NC}_{12}\text{H}_{23})]$  (14.2 g, 0.043 mol).

Part 4.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{NC}_{12}\text{H}_{23})]$  (7.7 g, 0.023 mol) was suspended in cold ether.  $\text{TiCl}_4 \cdot 2\text{Et}_2\text{O}$  (7.8 g, 0.023 mol) was slowly added and the mixture was allowed to stir overnight. ~~Dichloromethane was added and the mixture was allowed to stir overnight. The solvent was removed via vacuum.~~ Dichloromethane was added and the mixture was filtered through Celite. The dichloromethane was reduced in volume and petroleum ether was added to maximize precipitation. This mixture was then refrigerated for a short period of time prior to filtering off a yellow/green solid identified as  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$  (5.87 g, 0.013 mol).

#### Example C

Compound C: Part 1.  $\text{Me}_2\text{SiCl}_2$  (150 ml, 1.24 mol) was diluted with 200 ml of ether  $\text{Li}(\text{C}_{13}\text{H}_{27}) \cdot \text{Et}_2\text{O}$

(lithiated fluorene etherate, 28.2 g, 0.11 mol) was slowly added. The reaction was allowed to stir for -1 hr prior to removing the solvent via vacuum. Toluene was added and the mixture was filtered through Celite to remove the LiCl. The solvent was removed from the filtrate, leaving behind the off-white solid,  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)\text{Cl}$  (25.4 g, 0.096 mol).

Part 2.  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)\text{Cl}$  (8.0 g, 0.031 mol) was suspended in ether and <sup>THF</sup> in a ratio of 5:1.  $\text{LiHNC}_6\text{H}_{11}$  (3.25 g, 0.031 mol) was slowly added. The reaction mixture was allowed to stir overnight. After removal of the solvent via vacuum, toluene was added and the mixture was filtered through Celite to remove the LiCl. The filtrate was reduced in volume to give a viscous orange liquid. To this liquid which was diluted in ether, 43 ml of 1.4 M MeLi (0.060 mol) was added slowly. The mixture was allowed to stir overnight. The solvent was removed via vacuum to produce 13.0 g (0.031 mol) of  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)(\text{NC}_6\text{H}_{11})] \cdot 1.25 \text{ Et}_2\text{O}$ .

Part 3.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)(\text{NC}_6\text{H}_{11})] \cdot 1.25 \text{ Et}_2\text{O}$  (6.5 g, 0.015 mol) was dissolved in cold ether.  $\text{TiCl}_4 \cdot 2 \text{ Et}_2\text{O}$  (5.16 g, 0.017 mol) was slowly added. The mixture was allowed to stir overnight. The solvent was removed via vacuum and methylene chloride was added. The mixture was filtered through Celite to remove the LiCl. The filtrate was reduced in volume and petroleum ether was added. This was refrigerated to maximize precipitation prior to filtering off the solid. Since the solid collected was not completely soluble in toluene, it was mixed with toluene and filtered to remove the toluene insolubles. The filtrate was reduced in volume and petroleum ether was added to induce precipitation. The mixture was refrigerated prior to filtration. The red-brown solid

$\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{NC}_6\text{H}_{11})\text{TiCl}_2$  was isolated (2.3 g, 5.2 mmol).

Example D

B  
Compound D: Part 1.  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)\text{Cl}$  was prepared as described in Example C for the preparation of compound C,  
5 Part 1.

Part 2.  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)\text{Cl}$  (8.0g, 0.031 mol) was diluted in ether.  $\text{LiHN-t-Bu}$  (2.4 g, 0.030 mol) was slowly added and the mixture was allowed to stir overnight. The solvent was removed in vacuo and  
10 methylene chloride was added to precipitate out the  $\text{LiCl}$  which was filtered off. The solvent was removed from the filtrate leaving behind an oily yellow liquid identified as  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)(\text{NH-t-Bu})$  (8.8 g, 0.028 mol).

Part 3.  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)(\text{NH-t-Bu})$  (8.8 g, 0.028 mol)  
15 was diluted with ether.  $\text{MeLi}$  (1.4 M, 41 ml, 0.057 mol) was slowly added and the reaction was allowed to stir for about two hours. The solvent was removed via vacuum leaving behind an orange solid identified as  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})]\cdot\text{Et}_2\text{O}$ .

20 Part 4.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})]\cdot\text{Et}_2\text{O}$  (3.0 g, 0.008 mol) was dissolved in ether.  $\text{ZrCl}_4$  (1.84 g, 0.008 mol) was slowly added and the mixture was allowed to stir overnight. The solvent was removed via vacuum and a mixture of toluene and methylene chloride was added to  
25 precipitate the  $\text{LiCl}$  which was filtered off. The solvent was reduced in volume and petroleum ether was added to precipitate the product. The mixture was refrigerated to maximize precipitation prior to being filtered ~~off~~.  
B 30  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{ZrCl}_2$  was isolated as a yellow solid (1.9 g, 0.005 mol).

Example E

Compound E: Part 1.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{NC}_6\text{H}_{11})]\cdot 1.25 \text{ Et}_2\text{O}$  was prepared as described in Example C, Part 3 for the preparation of Compound C.

Part 2.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{NC}_6\text{H}_{11}) \cdot 1.25\text{Et}_2\text{O}]$  (3.25 g, 7.6 mmol) was dissolved in ether.  $\text{HfCl}_4$  (1.78, 5.6 mmol) was slowly added. The orange mixture was allowed to stir overnight. The solvent was removed via vacuum and a mixture of toluene and methylene chloride was added. The mixture was filtered through Celite to remove  $\text{LiCl}$ . The filtrate was reduced in volume and petroleum ether was added. This was refrigerated to maximize precipitation prior to filtering off the orange solid. After filtration of the mixture, the product  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{NC}_6\text{H}_{11})\text{HfCl}_2$  (1.9 g, 3.3 mmol) was isolated.

Example F

Compound F: Part 1.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})] \cdot \text{Et}_2\text{O}$  was prepared as described in Example D, Part 3 for the preparation of Compound D.

Part 2.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})] \cdot \text{Et}_2\text{O}$  (2.8 g, 7.3 mmol) was dissolved in ether.  $\text{HfCl}_4$  (2.35 g, 7.3 mmol) was slowly added and the reaction mixture was allowed to stir over night. The solvent was removed via vacuum and toluene was added. The mixture was filtered through Celite to remove  $\text{LiCl}$ . The filtrate was reduced in volume and petroleum ether was added. This was refrigerated to maximize precipitation prior to filtering off the pale orange solid. After filtration of the mixture, the product  $\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)(\text{N-t-Bu})\text{HfCl}_2$  (1.9 g, 3.5 mmol) was isolated.

Example G

Compound G: Part 1.  $\text{LiC}_9\text{H}_7$  (40 g, 0.33 mol, lithiated indene =  $\text{Li}(\text{Hind})$ ) was slowly added to  $\text{Me}_2\text{SiCl}_2$  (60 ml, 0.49 mol) in ether and  $\text{THF}$ . The reaction was allowed to stir for 1.5 hours prior to removing the solvent via vacuum. Petroleum ether was then added, and the  $\text{LiCl}$  was filtered off. The solvent was removed from the filtrate via vacuum, leaving behind the pale yellow liquid,  $(\text{Hind})\text{Me}_2\text{SiCl}$  (55.7 g, 0.27 mol).

Part 2. (Hind)Me<sub>2</sub>SiCl (17.8 g, 0.085 mol) was diluted with ether. LiHNC<sub>6</sub>H<sub>11</sub> (9.0 g, 0.086 mol) was slowly added and the mixture was allowed to stir overnight. The solvent was removed via vacuum and petroleum ether was added. The LiCl was filtered off and the solvent was removed via vacuum to give a viscous yellow liquid. To this liquid which was diluted in ether, 118 ml of 1.4 M MeLi (0.17 mol) was added and the mixture was allowed to stir for two hours. The solvent was removed via vacuum yielding the pale yellow solid, Li<sub>2</sub>[Me<sub>2</sub>Si(ind)(NC<sub>6</sub>H<sub>11</sub>)]·1/2Et<sub>2</sub>O (27.3 g, 0.085 mol).

Part 3. Li<sub>2</sub>[Me<sub>2</sub>Si(ind)(NC<sub>6</sub>H<sub>11</sub>)]·1/2Et<sub>2</sub>O (10.0 g, 0.031 mol) was suspended in ether. A small amount of TiCl<sub>4</sub>·2Et<sub>2</sub>O was added and the mixture was stirred for approximately five minutes. The mixture was then cooled to -30°C before adding the remaining TiCl<sub>4</sub>·2Et<sub>2</sub>O (total: 10.5 g, 0.031 mol). The mixture was allowed to stir overnight. The solvent was removed via vacuum and methylene chloride was added. The mixture was filtered through Celite and the brown filtrate was reduced in volume. Petroleum ether was added and the mixture was refrigerated to maximize precipitation. A brown solid was filtered off which was mixed in hot toluene and filtered through Celite to remove the toluene insolubles. Petroleum ether was added to the filtrate and the mixture was again refrigerated prior to filtering off the solid. This solid was recrystallized twice; once from ether and petroleum ether and once from toluene and petroleum ether. The last recrystallization isolated the pale brown solid, Me<sub>2</sub>Si(ind)(NC<sub>6</sub>H<sub>11</sub>)TiCl<sub>2</sub> (1.7 g, 4.4 mmol).

#### Example H

Compound H: Part 1. Me<sub>2</sub>Si(MeC<sub>5</sub>H<sub>4</sub>)Cl was prepared as described in Example B, Part 1 for the preparation of Compound B.

Part 2.  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)\text{Cl}$  (11.5 g, 0.067 mol) was diluted with ether.  $\text{LiHN-2,6-i-Pr}_2\text{C}_6\text{H}_3$  (12.2 g, 0.067 mol) was slowly added. The mixture was allowed to stir overnight. The solvent was removed via vacuum and a mixture of toluene and dichloromethane was added to precipitate the  $\text{LiCl}$ . The mixture was filtered and the solvent was removed from the filtrate leaving behind the viscous yellow liquid,  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HN-2,6-i-Pr}_2\text{C}_6\text{H}_3)$ . Assuming a -95% yield, 90 ml of  $\text{MeLi}$  (1.4 M in ether, 0.126 mol) was slowly added to a solution of  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HN-2,6-i-Pr}_2\text{C}_6\text{H}_3)$  in ether. This was allowed to stir overnight. The solvent was reduced in volume and the mixture was filtered and the solid collected was washed with aliquots of ether, then vacuum dried. The product,  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{N-2,6-i-Pr}_2\text{C}_6\text{H}_3)]$ , was isolated (13.0 g, 0.036 mol).

Part 3.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{N-2,6-i-Pr}_2\text{C}_6\text{H}_3)]$  (7.0 g, 0.019 mol) was diluted in cold ether.  $\text{TiCl}_4 \cdot 2\text{Et}_2\text{O}$  (6.6 g, 0.019 mol) was slowly added and the mixture was allowed to stir overnight. The solvent was removed via vacuum. Dichloromethane was added and the mixture was filtered through Celite. The dichloromethane was reduced in volume and petroleum ether was added to maximize precipitation. This mixture was then refrigerated for a short period of time prior to filtering off an orange solid which was recrystallized from dichloromethane and identified as  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{N-2,6-i-Pr}_2\text{C}_6\text{H}_3)\text{TiCl}_2$  (1.75g, 4.1 mmol).

~~Examples 1-10 of Polymerization~~

Example I

Compound I: Part 1.  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)\text{Cl}$  was prepared as described in Example B, Part 1 for the preparation of compound B.

Part 2.  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)\text{Cl}$  (10.0 g, 0.058 mol) was diluted with ether.  $\text{LiHNC}_6\text{H}_{11}$  (6.1 g, 0.58 mol) was



3  
B  
B 5 slowly added and the mixture was allowed to stir overnight. The solvent was removed via vacuum and toluene was added to precipitate the LiCl. ~~The toluene was removed via vacuum and toluene was added to precipitate the LiCl.~~ The toluene was removed from the filtrate leaving behind a pale yellow liquid,  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HNC}_6\text{H}_{11})$ . The yield was assumed to be -95%. Based on this, two equivalents of MeLi (1.4 M in ether, 0.11 mol, 80 ml) was slowly added to an ether solution of  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HNC}_6\text{H}_{11})$ . This was stirred for a few hours before removing the solvent and isolating the product,  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{NC}_6\text{H}_{11})]$  (12.3 g, 0.050 mol).

10  
15 Part 3.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{NC}_6\text{H}_{11})]$  (7.25 g, 0.029 mol) was suspended in cold ether.  $\text{TiCl}_4 \cdot 2\text{Et}_2\text{O}$  (9.9 g, 0.029 mol) was slowly added and the mixture was allowed to stir overnight. The solvent was removed via vacuum. Dichloromethane was added and the mixture was filtered through Celite. The dichloromethane was reduced in volume and petroleum ether was added to maximize precipitation. This mixture was then refrigerated for a short period of time prior to filtering off a maize colored solid which was recrystallized from dichloromethane and identified as  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{NC}_6\text{H}_{11})\text{TiCl}_2$  (3.25 g, 9.2 mmol).

25 Example J

Compound J: Part 1.  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)\text{Cl}$  was prepared as described in Example B, Part 1 for the preparation of Compound B.

30 Part 2.  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)\text{Cl}$  (10.0 g, 0.059 mol) was diluted with ether.  $\text{LiHN}-2,5\text{-t-Bu}_2\text{C}_6\text{H}_3$  (12.2 g, 0.58 mol) was slowly added and the mixture was allowed to stir overnight. The solvent was removed via vacuum and toluene was added to precipitate the LiCl. The toluene was removed from the filtrate leaving behind a pale yellow liquid,  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HN}-2,5\text{-t-Bu}_2\text{C}_6\text{H}_3)$ . The yield

was assumed to be -95%. Based on this, two equivalents of MeLi (1.4 M in ether, 0.11 mol, 80 ml) was slowly added to an ether solution of  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_4)(\text{HN-2,5-t-Bu}_2\text{C}_6\text{H}_3)$ . This was stirred for a few hours before removing the solvent and isolating the product,  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{N-2,5-t-Bu}_2\text{C}_6\text{H}_3)]$  (7.4 g, 0.021 mol).

Part 3.  $\text{Li}_2[\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{N-2,5-t-Bu}_2\text{C}_6\text{H}_3)]$  (6.3 g, 0.018 mol) was suspended in cold ether.  $\text{TiCl}_4 \cdot 2\text{Et}_2\text{O}$  (6.0 g, 0.18 mol) was slowly added and the mixture was allowed to stir overnight. The solvent was removed via vacuum. Dichloromethane was added and the mixture was filtered through Celite. The dichloromethane was reduced in volume and petroleum ether was added to maximize precipitation. This mixture was then refrigerated for a short period of time prior to filtering off a solid which was recrystallized from dichloromethane giving an orange solid identified as  $\text{Me}_2\text{Si}(\text{MeC}_5\text{H}_3)(\text{N-2,5-t-Bu}_2\text{C}_6\text{H}_3)\text{TiCl}_2$  (2.4 g, 5.2 mmol).

Example 1

Polymerization-Compound A

Using the same reactor design and general procedure already described, <sup>IN U.S. PAT. NO. 5,055,438</sup> 400 ml of toluene, ~~100 ml of toluene,~~ 100 ml of propylene, 2.5 ml of 1.0 M MAO, and 1.58 mg of compound A (1.0 ml of 15.8 mg of compound a in 10 ml of toluene) were added to the reactor. The reactor was heated at 30°C and the reaction was allowed to run for 30 minutes followed by rapidly cooling and venting the system. the polymer was precipitated out and filtered off giving 0.7 g of crystalline polypropylene (MW = 169,500, MWD = 1.605, m = 0.725, r = 0.275, 115 chain defects/1000 monomer units).

Example 2

Polymerization - Compound B

Using the same reactor design and general procedure already described, 100 ml of toluene, 100 ml of

B  
5 propylene, 2.5 ml of 1.0 M MAO, and 0.92 mg of compound  
B (1.0 ml of 9.2 mg of compound B in 10 ml of toluene)  
were added to the reactor. The reactor was heated at  
30°C <sup>and</sup> ~~and~~ the reaction was allowed to run for 30 minutes  
followed by rapidly cooling and venting the system. The  
polymer was precipitated out and filtered off giving 0.5  
g of crystalline polypropylene (MW = 279,800, MWD =  
1.823,  $m = 0.547$ ,  $r = 0.453$ , 180 chain defects/1000  
monomer units) in addition to 0.2 g of amorphous  
10 polypropylene.

Example 3

Polymerization - Compound C

15 Using the same reactor design and general procedure  
already described, 100 ml of toluene, 100 ml of  
propylene, 5 ml of 1.0 M MAO, and 2.46 mg of compound C  
(2 ml of 12.3 mg of compound C in 10 ml of toluene) were  
added to the reactor. The reactor was heated at 30°C and  
the reaction was allowed to run for 1 hour, followed by  
rapidly cooling and venting the system. The polymer was  
20 precipitated out and filtered off giving 2.2 g of  
crystalline polypropylene (MW = 29,000, MWD = 2.673,  $m =$   
 $0.356$ ,  $r = 0.641$ , 110.5 chain defects/1000 monomer units,  
 $mp = 143^{\circ}\text{C}$ ) and a trace amount of amorphous polypropylene  
which was isolated from the filtrate.

Example 4

Polymerization - Compound D

25 Using the same reactor design and general procedure  
already described, 100 ml of toluene, 200 ml of  
propylene, 5 ml of 1.0 M MAO, and 6.4 mg of compound D (5  
30 ml of 12.4 mg of compound D in 10 ml of toluene) were  
added to the reactor. The reactor was heated at 30°C and  
the reaction was allowed to run for one hour, followed by  
rapidly cooling and venting the system. The polymer was  
precipitated out and filtered off giving 1.4 g of  
75 crystalline polypropylene (MW = 76,900, MWD = 1.553,  $m =$

0.982,  $r = 0.18$ , 9.1 defects/1000 monomer units,  $mp = 145^{\circ}C$ ) and trace amounts of amorphous polypropylene which was isolated from the filtrate.

Example 5

5 Polymerization - Compound E

Using the same reactor design and general procedure already described, 100 ml of toluene, 200 ml of propylene, 5.0 ml of 1.0 M MAO, and 8.0 mg of compound E (5.0 ml of 16.0 mg of compound E in 10 ml of toluene)  
10 were added to the reactor. The reactor was heated at  $30^{\circ}C$  and the reaction was allowed to run for 1 hour followed by rapidly cooling and venting the system. The polymer was precipitated out and filtered off giving 2.3 g of crystalline polypropylene ( $MW = 68,600$ ,  $MWD = 1.718$ ,  
15  $m = 0.945$ ,  $r = 0.055$ , 21.6 chain defects/1000 monomer units,  $mp = 149^{\circ}C$ ).

Example 6

Polymerization - Compound F

Using the same reactor design and general procedure  
20 already described, 100 ml of hexane, 500 ml of propylene, 10.0 ml of 1.0 M MAO, and 3.4 mg of compound F (2.0 ml of 17.0 mg of compound F in 10 ml of toluene) were added to the reactor. The reactor was heated at  $30^{\circ}C$  and the reaction was allowed to run for 2.5 hours followed by  
25 rapidly cooling and venting the system. The polymer was precipitated out and filtered off giving 3.1 g of crystalline polypropylene ( $MW = 70,600$ ,  $MWD = 1.726$ ,  $m = 0.858$ ,  $r = 0.143$ , 45.2 chain defects/1000 monomer units,  $mp = 144^{\circ}C$ ).

30 Example 7

Polymerization - Compound G

Using the same reactor design and general procedure already described, 200 ml of toluene, 200 ml of propylene, 5.0 ml of 1.0 M MAO, and 5.5 mg of compound G  
35 (5.0 ml of 11.0 mg of compound G in 10 ml of toluene)

were added to the reactor. The reactor was heated at 30°C and the reaction was allowed to run for 1.0 hour followed by rapidly cooling and venting the system. The polymer was precipitated out and filtered off giving 2.4 g of crystalline polypropylene (MW = 71,300, MWD = 1.812,  $m = 0.866$ ,  $r = 0.134$ , 52 chain defects/1000 monomer units, mp = 147°C) and trace amounts of amorphous polymer.

#### Example 8

##### Polymerization - Compound H

Using the same reactor design and general procedure already described, 100 ml of toluene, 100 ml of propylene, 2.5 ml of 1.0 M MAO, and 0.86 mg of compound H (1.0 ml of 8.6 mg of compound H in 10 ml of toluene) were added to the reactor. The reactor was heated at 30°C and the reaction was allowed to run for one hour followed by rapidly cooling and venting the system. The polymer was precipitated out and filtered off giving 2.8 g of crystalline polypropylene (MW = 170,300, MWD = 2.275,  $m = 0.884$ ,  $r = 0.116$ , 46.5 chain defects/1000 monomer units, mp = 151°C).

#### Example 9

##### Polymerization - Compound I

Using the same reactor design and general procedure already described, 100 ml of toluene, 100 ml of propylene, 2.5 ml of 1.0 M MAO, and 0.70 mg of compound I (1.0 ml of 7.0 mg of compound I in 10 ml of toluene) were added to the reactor. The reactor was heated at 30°C and the reaction was allowed to run for one hour followed by rapidly cooling and venting the system. The polymer was precipitated out and filtered off giving 2.3 g of crystalline polypropylene (MW = 145,500, MWD = 3.551,  $m = 0.860$ ,  $r = 0.140$ , 57.1 chain defects/1000 monomer units, mp = 151°C).

Example 10

Polymerization - Compound J

Using the same reactor design and general procedure already described, 100 ml of toluene, 100 ml of propylene, 2.5 ml of 1.0 M MAO, and 1.0 mg of compound J (1.0 ml of 10.0 mg of compound J in 10 ml of toluene) were added to the reactor. The reactor was heated at 30°C and the reaction was allowed to run for one hour followed by rapidly cooling and venting the system. The polymer was precipitated out and filtered off giving 1.4 g of crystalline polypropylene (MW = 211,400, MWD = 2.734,  $m = 0.750$ ,  $r = 0.250$ , 97.3 chain defects/1000 monomer units,  $mp = 144^{\circ}C$ ).

Table 2 summarizes the polymerization conditions employed and the properties obtained in the product polymers as set forth in Examples 1-10 above.

TABLE 2

Exp. No.	Transition Metal Component (TMC)		Methylalumoxane MAO	RXN		Yield (g)	Ac-tivity g polymer/hr	MP (°C.)		MWD		MW		m		mmmm		r		Chain Defects/1000 Monomer Units
	Type	mmole		MAO	mmole			TMC	Time (hr)	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	na <sup>a</sup>	
1	A	3.30 × 10 <sup>-3</sup>	2.5	760	0.5	0.7	424	169,500	1.605	na <sup>a</sup>	0.725	0.446	0.275	0.022	115					
2	B	2.11 × 10 <sup>-3</sup>	2.5	1200	0.5	0.5	474	279,800	1.823	na <sup>a</sup>	0.547	0.227	0.453	0.063	180					
3	C	5.61 × 10 <sup>-3</sup>	5.0	900	1.0	2.2	392	29,000	2.673	143	0.359	0.151	0.641	0.353	110.5					
4	D	1.41 × 10 <sup>-3</sup>	5.0	360	1.0	1.4	100	76,900	1.553	145	0.982	0.934	0.018	0.000	9.1					
5	E	1.41 × 10 <sup>-3</sup>	5.0	360	1.0	2.3	164	68,600	1.718	149	0.945	0.883	0.055	0.007	21.6					
6	F	6.26 × 10 <sup>-3</sup>	10.0	1600	2.5	3.1	198	70,600	1.726	144	0.858	0.756	0.143	0.036	45.2					
7	G	1.42 × 10 <sup>-3</sup>	5.0	350	1.0	2.4	169	71,300	1.812	147	0.866	0.747	0.134	0.016	52					
8	H	2.00 × 10 <sup>-3</sup>	2.5	1250	1.0	2.8	1400	170,300	2.275	151	0.884	0.774	0.116	0.012	46.5					
9	I	1.99 × 10 <sup>-3</sup>	2.5	1250	1.0	2.3	1156	145,500	3.551	151	0.860	0.718	0.140	0.013	57.1					
10	J	2.18 × 10 <sup>-3</sup>	2.5	1150	1.0	1.4	642	211,400	2.734	144	0.750	0.535	0.250	0.031	97.3					

<sup>a</sup>Data not available.

B By appropriate selection of (1) Group IV<sup>B</sup> transition metal component for use in the catalyst system; (2) the type and amount of alumoxane used; (3) the polymerization diluent type and volume; and (4) reaction temperature, one may tailor the product polymer to the weight average molecular weight value desired while still maintaining the molecular weight distribution <sup>at</sup> to a value below about 4.0.

10 The stereochemical control of the polymer formed is highly dependent on the exact structure of the transition metal component. Those transition metal components containing zirconium or hafnium (M = Zr or Hf) appear to have greater stereoregularity (fewer chain defects) than ~~these~~ <sup>those</sup> containing titanium (M = Ti). By appropriate selection of the transition metal component of the catalyst system a wide variety of crystalline poly- $\alpha$ -olefins with differing stereochemical structure are possible.

20 The resins that are prepared in accordance with this invention can be used to make a variety of products including films and fibers.

25 The invention has been described with reference to its preferred embodiments. Those of ordinary skill in the art may, upon reading this disclosure, appreciate changes or modifications which do not depart from the scope and spirit of the invention as described above or claimed hereafter.